

HIGH TEMPERATURE PROTECTIVE  
COATINGS FOR REFRACTORY METALS

by

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UNION CARBIDE CORPORATION  
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# HIGH TEMPERATURE PROTECTIVE COATINGS FOR REFRACTORY METALS

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## I. INTRODUCTION

The research performed under Contract NASw-1405 is a continuation of work initiated under NASA Contract NASw-1030<sup>(1)</sup>. The contract has been extended for one year (to April 21, 1968) with slight modifications in the program objectives. The major objectives of the present program are: 1) to study the rates of interdiffusion of iridium with the refractory metals tungsten, molybdenum, and niobium and, 2) to examine the mechanical behavior of coated and heat-treated subsized specimens. The fused salt electrodeposition of iridium onto the refractory metals will be deemphasized.

This report summarizes the research effort for the period 21 January 1967 to 21 April 1967. A complete description of the materials used, methods of sample preparation, and the diffusion and electroplating apparatus were given in previous reports.<sup>(2)</sup>

## II. SUMMARY

During the present report period, several iridium-molybdenum diffusion couples were hot pressed. Sections of the hot-pressed diffusion couples were heat-treated at 1300°, 1530°, 1710°, and 1900°C. Some success was achieved in developing a two step color tinting method for revealing the molybdenum-iridium reaction zone. Select specimens were also examined with an electron microprobe analyzer. No additional work was done with the tungsten-iridium system during this report period.

Several niobium and tantalum sheet samples were electroplated with nickel from an aqueous electrolyte. Iridium was then electroplated, from the molten cyanide electrolyte, on to the nickel. No additional iridium electroplating

is anticipated at the present time. Sections of the dual-coated samples will be examined metallographically, and other sections will be heat treated to determine the effect of the nickel inner layer on the behavior of the systems.

### III. PROGRESS

#### A. Diffusion Studies

The objective of this portion of the program is to obtain the data needed to determine the life expectancy of an iridium coating consumed by both surface oxidation and the growth of the reaction zone formed between iridium and the refractory metals. The oxidation behavior of pure iridium has been studied.<sup>(3)</sup> Because of the irregularity of the total reaction zone interfaces, the observed preferential diffusion of iridium along the molybdenum grain boundaries, and the difficulties experienced in optically resolving the total reaction zone in both the molybdenum-iridium and tungsten-iridium systems, precise data on the growth of the reaction zone will be difficult to obtain in polycrystalline samples. Consequently, a direct determination of the decrease in thickness of iridium resulting from the formation of the reaction zone may yield more meaningful data. An effort will be made to re-examine the systems studied thus far by determining the iridium remaining (or consumed) as a function of time and temperature. In addition, annealed specimens will be examined with the microbend tester to determine the effect of the reaction zone on the mechanical behavior of the coating substrate systems.

1. Molybdenum-Iridium System: - Three additional (for a total of five) molybdenum-iridium diffusion couples were prepared by the hot-pressing techniques previously described. Sections of the hot-pressed samples were metallographically polished and etched and other sections were heat-treated. The preliminary estimate of the total reaction zone thickness was made by direct measurement with a microscope using a calibrated eye piece. The results are given in Table I. No evidence of intermetallic compound formation was observed in any of the hot-pressed specimens and the iridium and molybdenum were well bonded together. Figure 1 is a photomicrograph of a section of hot-pressed sample HP-3M. It is typical of the hot-pressed samples showing molybdenum

TABLE I  
DIFFUSION DATA FOR THE MOLYBDENUM-IRIDIUM SYSTEM

Sample No.	Optical Pyrometer Temperature °C	Thermocouple mV	Heat Treat Time, hrs.	Total Reaction Zone, Width, $\mu$
HP-1M*				0
HP-2M*				0
HP-3M*				0
HP-4M*				0
HP-5M*				0
HP-1M-1300-1	1292 $\pm$ 10	22.65 $\pm$ 0.01	1.0	4.2
HP-1M-1300-2	1292 $\pm$ 10	22.65 $\pm$ 0.01	2.0	--- **
HP-1M-1300-3	1292 $\pm$ 10	22.65 $\pm$ 0.01	4.0	7.0
HP-1M-1300-4	1292 $\pm$ 10	22.65 $\pm$ 0.01	8.0	9.1
HP-1M-1300-5	1292 $\pm$ 10	22.65 $\pm$ 0.01	16.0	11.2
HP-3M-1530-1	1527 $\pm$ 10	26.58 $\pm$ 0.01	1.0	14.0
HP-3M-1530-2	1527 $\pm$ 10	26.58 $\pm$ 0.01	2.0	19.6
HP-3M-1530-3	1527 $\pm$ 10	26.58 $\pm$ 0.01	4.0	25.2
HP-3M-1530-4	1527 $\pm$ 10	26.58 $\pm$ 0.01	8.4	(16.8)**
HP-3M-1530-5	1527 $\pm$ 10	26.58 $\pm$ 0.01	16.2	(28.0)**
HP-4M-1710-1	1695 $\pm$ 10	29.15 $\pm$ 0.03	1.0	16.8
HP-4M-1710-2	1695 $\pm$ 10	29.15 $\pm$ 0.03	2.0	(16.8)**
HP-2M-1710-3	1695 $\pm$ 10	29.15 $\pm$ 0.03	4.0	(24.0)**
HP-4M-1710-4	1695 $\pm$ 10	29.15 $\pm$ 0.03	8.0	(30.8)**
HP-5M-1900-1	1895 $\pm$ 10	31.94 $\pm$ 0.02	0.4	8.4
HP-4M-1900-2	1895 $\pm$ 10	31.94 $\pm$ 0.02	2.0	(19.6)**

\* Sections of the hot-pressed samples.

\*\* Delamination before or during heating or annealing.

grains but no grain structure in the iridium phase and no observable reaction zone.

A double etch method was developed that color tints the molybdenum-rich intermediate phase and provides color contrast to the molybdenum grains without severely attacking the grain boundaries. Neither etchant reveals the iridium-rich intermediate phase vividly. However, there is a sufficient increase in contrast between the iridium and the iridium rich intermediate phase, which is also bireflectant under polarized light, to clearly reveal the interfacial boundary under the microscope. For purposes of photography, a further increase in contrast would be desirable. A description of the polishing and etching procedure follows: Specimens mounted in epoxy resin are given a final polish with one-micron diamond paste on a Texmet polishing cloth. The polished samples are first electrolytically etched for approximately five seconds, anodically at a DC potential of two volts, in a solution containing 300 ml water and 30 ml sodium hydroxide. The etchant color tints the molybdenum rich intermediate phase and attacks the molybdenum grain boundaries. The sample is then electrolytically etched for approximately five seconds, anodically at a DC potential of two volts, in a solution of 150 ml water and 25 ml phosphoric acid. The second etchant provides color to the molybdenum grain surface without severely attacking the grain boundaries. Neither etchant reacts noticeably with iridium.

Figures 2, 3, and 4 are photomicrographs of samples HP-1M-1300-5, HP-3M-1530-2, and HP-4M-1710-4, respectively, taken at a magnification of 1000X. In these photomicrographs, the molybdenum grains, the molybdenum-rich intermediate phase, and the light (void of structural details) iridium phase can readily be seen. Structural details are not observable in the iridium-rich intermediate phase, and there is very little contrast difference between this phase and the iridium. In addition, Figures 2 and 3 indicate that iridium may be preferentially diffusing along the molybdenum grain boundaries.

In the photomicrograph of Figure 2, two intermetallic phases seem to be present. Giessen, Jaehnigen, and Grant <sup>(4)</sup> indicated that the three phases  $\text{Mo}_3\text{Ir}$ ,  $\text{MoIr}$ , and  $\text{MoIr}_3$  are present at 1300°C. With reference to the same publication, at 1530°C the above phases and an  $\epsilon$ -phase are present. The  $\epsilon$ -phase can undergo two eutectoid decomposition reactions on cooling (i. e.,  $\epsilon \rightarrow \text{Mo}_3\text{Ir} + \text{MoIr}$  and  $\epsilon \rightarrow \text{MoIr} + \text{MoIr}_3$ ). Similarly at 1710°C, the phases  $\text{Mo}_3\text{Ir}$ ,  $\epsilon$ , and  $\alpha$   $\text{MoIr}_3$  are

present and the  $\epsilon$  -phase decomposes on cooling.

In an effort to determine what, if any, features of the photomicrographs were artifacts, sections of the above samples were examined with an electron microprobe analyzer. This work was carried out at the Research Laboratory of the Mining and Metals Division of Union Carbide Corporation at Niagara Falls, New York. Figure 5 is an X-ray line scan for iridium in a polished section of sample HP-3M. The grain structures within the iridium (the dark phase) and molybdenum (light phase) are not discernible. The overall specimen image and the X-ray line scan do not reveal any intermediate compound formation, substantiating the findings of the photomicrograph of Figure 1. The electron microprobe micrographs of Figures 6 through 10 may be compared with the photomicrograph of Figure 3, since they are all of sample HP-3M-1530-2. Figure 6 shows an X-ray scan for iridium. Although this sample has a rather wide band of reaction products, this type of analysis did not detect the different concentrations of iridium in the various intermetallic compounds. The electron scanning image of Figure 7 shows the reaction zone structural details obtainable with the microprobe analyzer. No structural details can be observed in either the iridium or molybdenum (light phase). However, the intermediate phases present in the reaction zone are readily detected, including the iridium rich phases that are difficult to detect in the photomicrograph of Figure 3. The scanning image indicates that there may be as many as five intermediate phases in the reaction zone. Figure 8 shows X-ray line scans for both iridium and molybdenum in which the reaction zone interfaces adjacent to both the iridium and molybdenum are easily located. The intermetallic phases present in the reaction zone could not be identified. Figures 9 and 10 show some structural details in iridium and molybdenum respectively. In addition, Figure 10 includes an iridium line scan that detected iridium in the molybdenum grain boundaries but not in the grains themselves. An iridium point count in the molybdenum grains and in the boundaries separating the grains definitely indicated the presence of iridium within the boundaries but none within the grains.

Similar electron microprobe analyses were conducted on sections of samples HP-3M-1530-3, HP-4M-1900-2, HP-1M-1300-5, and HP-4M-1710-4.



Figure 1. Photomicrograph of hot-pressed sample HP-3M, 1000X

N 11665

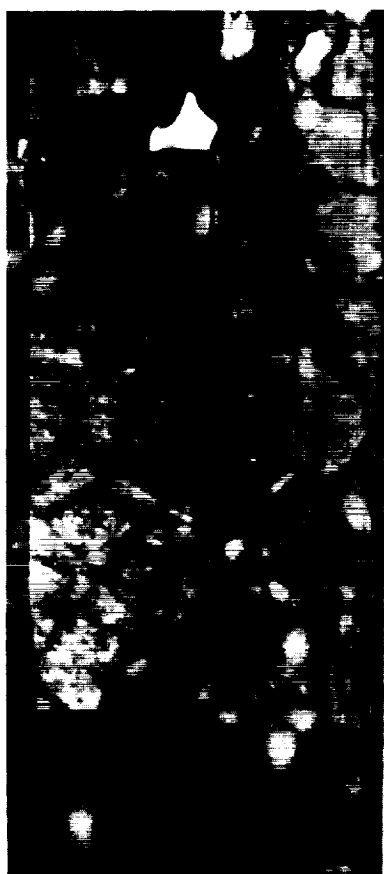




Figure 2. Photomicrograph of annealed sample HP-1M-1300-5, 1000X.

N-11666

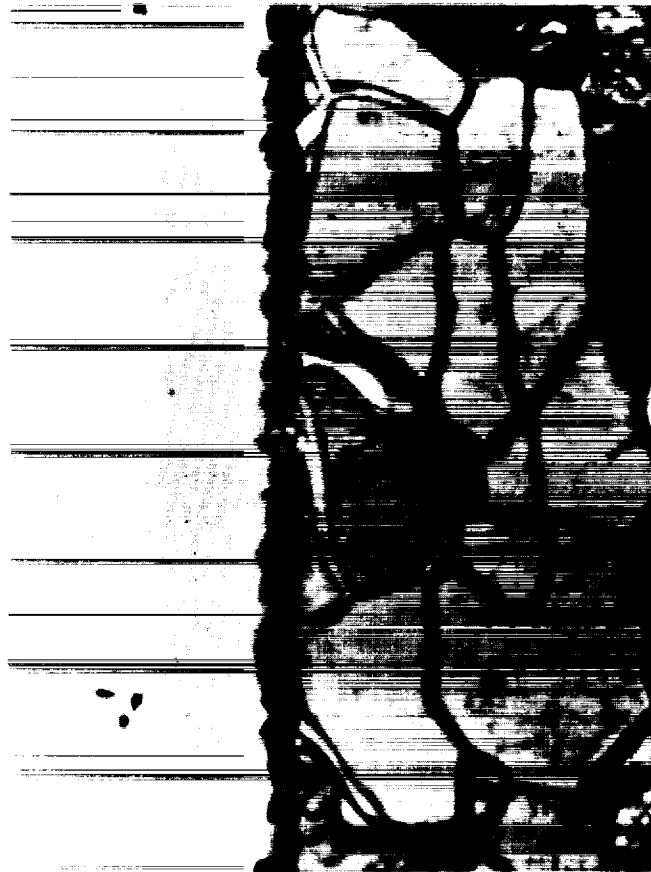


Figure 3. Photomicrograph of annealed sample HP-3M-1530-2  
1000X.

N-11667



Figure 4. Photomicrograph of annealed sample HP-4M-1710-4  
1000X.

N-11668

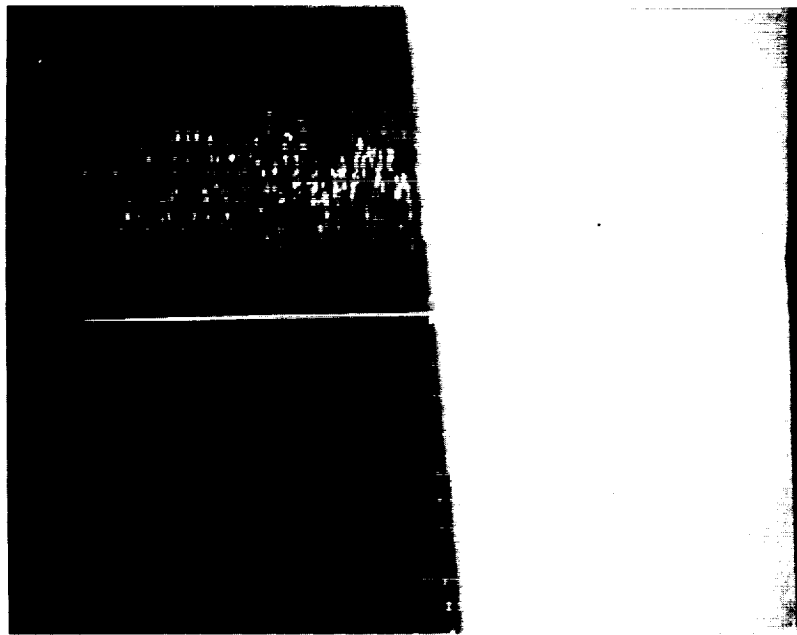


Figure 5. Electron microprobe X-ray line scan for iridium in sample HP-3M, 1250X.

N 11669

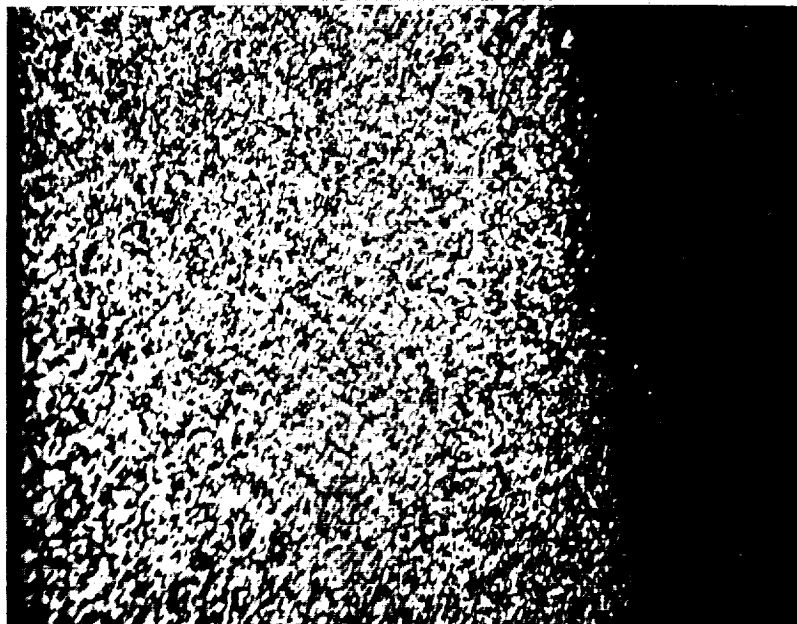


Figure 6. Electron microprobe X-ray scan for iridium in sample HP-3M-1530-2, 1250X.

N 11670

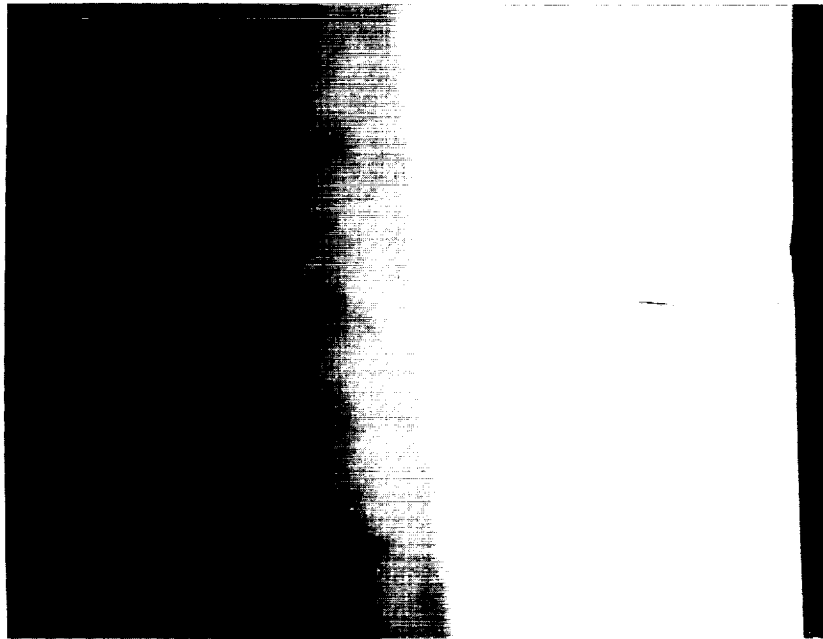


Figure 7. Electron microprobe electron scanning image of sample HP-3M-1530-2, 1250X.

N 11671

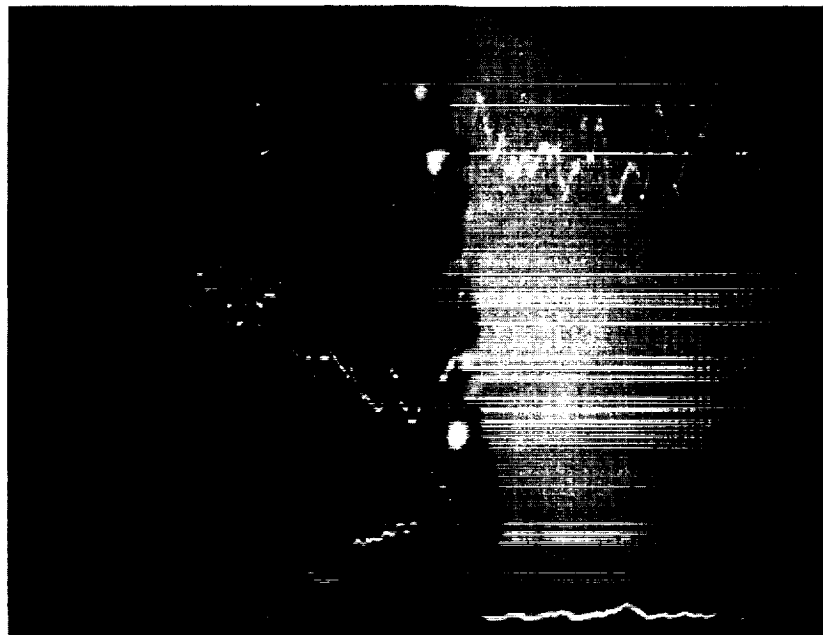


Figure 8. Electron microprobe iridium and molybdenum X-ray line scans in sample HP-3M-1530-2, 1250X.

N 11672

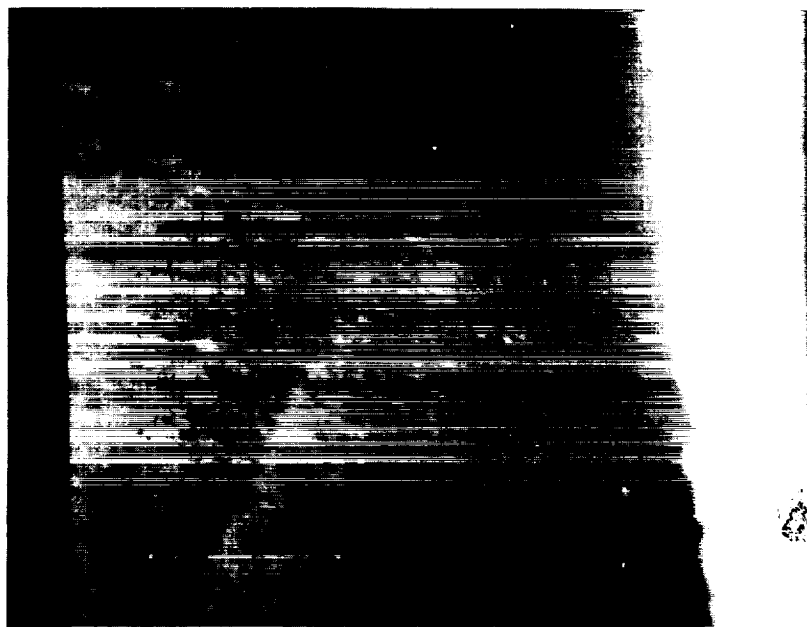


Figure 9. Electron microprobe electron scanning image for iridium structural details in sample HP-3M-1530-2, 1250X.

N 11673

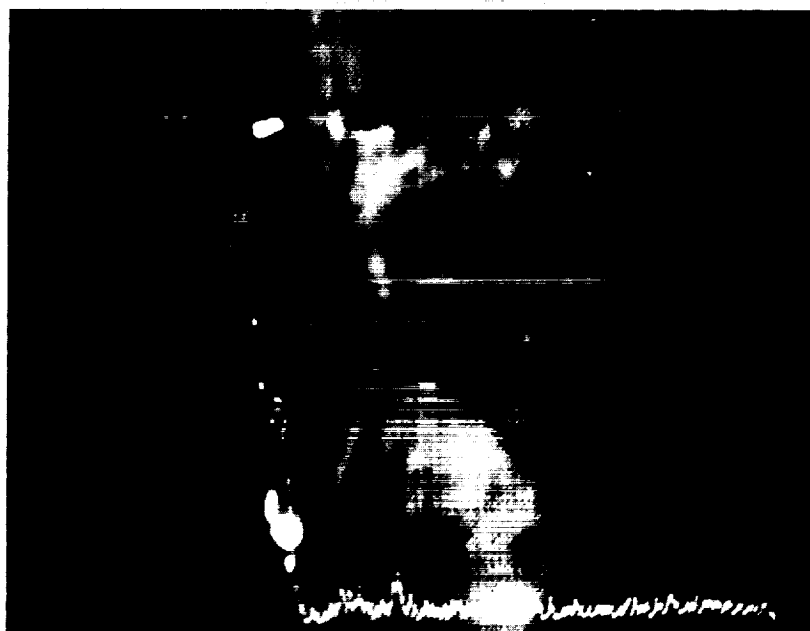


Figure 10. Electron microprobe electron scanning image for molybdenum structural details and an iridium X-ray line scan of sample HP-3M-1530-2, 1250X.

N 11674

To summarize, the microprobe analyses showed that some preferential grain boundary diffusion of iridium in molybdenum occurred. Although grain boundary diffusion may not occur appreciably at all annealing temperatures, preferential grain orientation or grain boundary diffusion results in the formation of highly irregular reaction zone interfacial boundaries.

Partial delamination was observed in several samples annealed at 1530°C and above. Particularly noteworthy was sample HP-4M-1710-2. This sample was a section of HP-4M-1710-1 that was heated for one additional hour at the same temperature. After annealing, the total reaction zone width in the delaminated sample was the same as before the second anneal. Either the process of sectioning HP-4M-1710-1 produced a fracture or the thermal shock of heating rapidly to the annealing temperature produced a break in the reaction zone.

A malfunction by the control unit while calibrating a new thermocouple resulted in extensive damage to the heat-treating apparatus. A new tungsten crucible was fabricated by electrodeposition from a molten salt bath, and the heat-treating apparatus is being repaired.

2. Tungsten-Iridium System: No additional work was done with the tungsten-iridium system during this period.

#### B. Fused-Salt Electroplating of Iridium

Several niobium and tantalum sheet samples were electroplated with less than 0.1 mil thick nickel from a commercially available nickel sulfamate electrolyte. Iridium was then deposited from the molten cyanide electrolyte previously described. Sections of the dual-coated samples will be heat treated to determine the effect of the nickel inner layer on the behavior of the systems.

dd



## REFERENCES

1. Criscione, J. M., Rexer, J., and Fenish, R. G., "High Temperature Protective Coatings for Refractory Metals", under Contract NASw-1030.
2. Rexer, J., "High Temperature Protective Coatings for Refractory Metals", Progress Report No. 2 under Contract NASw-1405.
3. Rexer, J., "The Effect of Gas Velocity on the Oxidation of Iridium", Paper presented at 4th AIME Refractory Metals Symposium, 4 Oct. 1954, French Lick, Indiana.
4. Giessen, B. C., Jaehnigen, U., and Grant, N. J., J. Less Common Metals 10, 147 (1965).

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